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Thermal energy storage implementation using phase change materials for solar cooling and refrigeration applications

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Abstract

The final goal of this study is to implement and to test a thermal energy storage (TES) system using different phase change materials (PCM) for solar cooling and refrigeration applications. A high temperature pilot plant able to test different types of TES systems and materials was designed and built at the University of Lleida (Spain). This pilot plant is composed mainly by three parts: heating system, cooling system, and different storage tanks. The pilot plant uses synthetic thermal oil as heat transfer fluid (HTF) and has a working temperature range from 100 °C to 400 °C. Two different PCM were selected after a deep study of the requirements of a real solar cooling plant and the available materials in the market, finally d-mannitol with phase change temperature of 167 °C and hydroquinone which has a melting temperature of 172.2 °C were used.

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Keywords: Thermal energy storage; solar cooling and refrigeration; pilot plant; high temperature

1. Introduction

Nowadays, solar cooling and refrigeration technology have become vital for both human comfort and temperature sensitive food conservation since the energy used, solar energy, is the cheapest and most extensively available renewable energy. Moreover, there is an urgent need to develop and promote environmentally benign sustainable cooling technologies because the conventional cooling technologies consume high energy and cause peak loads leading to negative environmental impacts [1].

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Since solar energy is time dependent, the main disadvantage of this energy resource is the mismatch between the energy supply and the energy demand. In solar vapor absorption systems, the energy received from the solar collector is given as heat input to the generator; hence it has to assure a constant heat input to the absorption chiller during all the process. Therefore, when energy is available but cannot be given to the process, thermal energy storage (TES) may become an important issue. TES is a widely studied and used technology due to its potential load reduction, energy savings, and ability to overcome the disadvantage of the intermittent energy supply and demand [2-3]. Storage systems could be based on sensible, latent or thermo-chemical heat. Here, a TES system based on phase change materials (PCM) which absorb or release heat when the PCM undergoes a phase change is analyzed. Moreover, PCM systems have high-energy storage capacity and isothermal behavior during both charging and discharging processes. There are different ways through which heat energy can be stored [1]:

- External heat storage:
 - o Storing hot energy to supply the generator.
 - o Storing of produced cool energy.
- Internal heat storage:
 - o In external thermal storage systems, the HTF from the solar collectors could be circulated to the hot thermal storage tank to store energy for later use.

The temperature requirement for a vapor absorption system obviously depends on each system; however, heat has to be supplied within a narrow operating temperature range of 5-10 °C for better performance. Therefore, in this study an internal TES system is developed in order to supply to the absorption chiller constant heat transfer fluid (HTF) temperatures even if the coming temperature from the solar collectors is too high or too low.

Many researchers have dealt with both experimental and numerical analysis of different configurations of TES systems using PCM as the storage media for different applications. Medrano et al. [4] experimentally investigated the heat transfer process during the melting and solidification RT35 as PCM in five small heat exchangers. The highest average thermal power was obtained for the compact heat exchanger which was a shell-and-tube which incorporated fins. Later on, Adine and Qarnia [5] presented a numerical analysis of the thermal behavior of a shell-and-tube PCM system comparing the utilization between one and two PCM. Similarly, Trp et al. [6] analyzed numerically and experimentally the transient phenomenon during both charging and discharging processes of the shell-and-tube latent energy storage system using paraffin as PCM. The authors concluded a general statement saying that the selection of the operating conditions and geometric parameters dimensions depends on the required heat transfer rate and the time in which the energy has to be stored or delivered. Moreover, and due to the solar radiation intensity variation over time, the phase change process can occur under the non-steady-state inlet boundary conditions. Tao and He [7] performed a numerical study on TES performance of PCM using a shell-and-tube unit under non-steady-state inlet boundary conditions. Their main conclusion was that when the average HTF inlet temperature is fixed at a constant value, the melting time decreases with the increase of the initial inlet temperature.

Most of the researchers worked with PCM having low phase change temperature; however, some other investigations using PCM with higher melting point have been performed. Agyenim et al. [8] compared the performance of a multi-tube system with that of a single tube shell and tube system using a PCM with a phase change temperature of 117.7 °C. The main conclusion of their study was that the multi-tube system improved the heat transfer rate during charging, and produced an output temperature suitable to operate the absorption cooling system, but showed large subcooling effect. Moreover, an eutectic mixture of $\text{KNO}_3/\text{NaNO}_3$ as PCM with a melting temperature of 221 °C in a storage prototype with an expanded graphite sandwich configuration for direct steam generation in solar thermal power plants was experimentally tested by Bayón et al. [9].

In the study presented here, a TES tank was developed and tested with two different PCM for its use in solar cooling and refrigeration applications. The TES tank, is placed between the solar collectors and the cooling machine (by absorption, adsorption, or desiccant cooling technology) to store the heat produced by the solar collectors at the temperature range between 140 and 200 °C, and to release it at the require time, temperature, and power, to the cooling machine. The main objective of this paper is to compare two PCM (hydroquinone and d-mannitol) which have different phase change temperatures and heats of fusion in a pilot plant built at the University of Lleida (Spain).

2. Materials and methodology

2.1 Materials

The first stage in the materials selection was to select a temperature range adequate for the implementation of TES systems in a solar cooling plant. The temperature range of the storage was 140–200 °C, where 200 °C represents the maximum temperature leaving the solar collectors (in this case Fresnel collectors were considered) and 140 °C the minimum inlet temperature in the absorption chiller. Obviously, another requirement was a heat of fusion higher than 150 kJ/kg. Moreover, mechanical, chemical, economic, and environmental properties of the candidates (as volumetric variation between solid and liquid, chemical stability, vapor pressure, toxicity, compatibility with the container material, price, availability, etc.) were taken into account in the selection process.

First, different PCM with phase change temperature in the range for solar cooling applications were selected as candidates from literature review [10–11]. Table 1 shows the data available in the literature and the data from the tests performed in our laboratories (phase change temperature and heat of fusion) of the different PCM candidates analyzed. The first PCM selected was hydroquinone due to its high phase change enthalpy in both literature and DSC testing and also to the little subcooling effect seen at lab scale. As it will be seen later, no subcooling effect was detected when hydroquinone was placed in a pilot plant tank scale; hence the authors think that the subcooling effect could be mitigated in real applications. D-mannitol was selected as PCM for its high heat of fusion even though the material presented high subcooling at lab scale. Both of them were tested in the pilot plant at the University of Lleida.

Table 1. List of materials tested with possibilities to work as PCM in solar cooling applications

Material	Literature phase change temperature [°C]	Experimental phase change temperature [°C]	Literature phase change enthalpy [kJ/kg]	Experimental phase change enthalpy [kJ/kg]
Salicylic acid	159	159.1 (m) / 111.3 (s)	199	161.5 (m) / 109.4 (s)
Benzanilide	161	163.6 (m) / 136.1 (s)	162	138.9 (m) / 129.4 (s)
D-mannitol	167	166.8 (m) / 117.0 (s)	316	260.8 (m) / 214.4 (s)
Hydroquinone	172.4	172.5 (m) / 159.5 (s)	258	235.2 (m) / 178.7 (s)
Potassium thiocynate	173	176.6 (m) / 156.9 (s)	280	114.4 (m) / 112.5 (s)

2.2 Experimental set-up and methodology

The high temperature pilot plant is composed by three main parts: (1) the heating system, consisting of a 24 kWe electrical boiler which heats the HTF up simulating the solar energy source in a real installation, (2) the cooling system, which is an air-HTF heat exchanger of 20 kWth to simulate the cooling technology, and (3) different storage tanks. Here, the tank analyzed is a shell-and-tubes heat

exchanger; the PCM is located in the shell part and the HTF circulated through the 49 tubes. Fig. 1 shows a general view of the equipment built at University of Lleida and the most important parts of it.

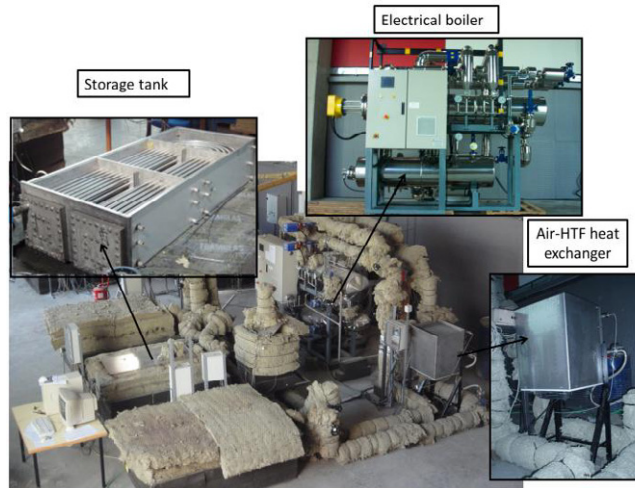


Fig. 1. High temperature pilot plant built at the University of Lleida

The HTF inlet, the storage tanks temperature and HTF flow rate are controllable variables by the pilot plant users. In order to evaluate the behavior of the PCM in the storage tank 15 temperature sensors were inserted in the main part of the tank and close to the HTF tubes (from TPCM.1 to TPCM.15 in Fig. 2). Moreover, more temperature sensors were placed at the corners and the central part of the storage tank. Fig. 2 shows the TES tank used in the experimentation with the location of the PCM temperature sensors.

Even though the pilot plant enables different type of tests for high temperature TES systems, a charging and discharging process at constant HTF temperature was performed. Before the start of the experiment, a warming period was defined (initial boundary conditions). During this period, the PCM is heated up to the initial temperature of the experiment in order to reach a homogeneous initial state of the PCM that in the experimentation presented here is 145 °C (preparation of the charging process). Once the PCM in the storage tank reached the initial experiment temperature, the HTF is heated up outside the tank to 187 °C, and when this temperature is reached, the charging process starts (charging process). The temperature of the HTF in the tank inlet is nearly 187 °C, with a range of ± 1.5 °C during all the charging process. The charging process is stopped 5 hours after the temperature of the sensors installed in the body of the tank show that the melting temperature of both PCM is reached. Then, the charging process is stopped and the HTF is cooled down to 145 °C outside the tank (preparation of the discharging process). When this temperature is reached, the discharging process starts (discharging process). During all the discharging, the HTF is introduced in the storage tank at 145 °C. As in the charging process, discharge is stopped 5 hours after the PCM has reached the solidification temperature.

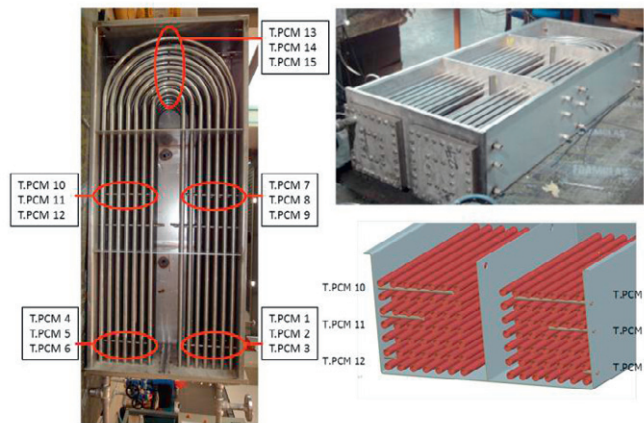


Fig. 2. Thermal Energy storage tank designed and built at the University of Lleida

3. Results

Fig. 3 and Fig. 4 show the evolution of the temperature of different parts of the storage material when hydroquinone and d-mannitol were used as PCM, respectively. In order to discuss the results, and for better understanding, only the PCM temperature at medium height of the tank (T.PCM 2, 5, 8, 11 and 14) are shown. Before the charging process, the PCM was homogeneously at 145 °C; the charging process was done at 187 °C while the discharging was done at a HTF temperature of 145 °C. Hydroquinone was the first PCM candidate analyzed. As it has been shown before, the DSC test showed some subcooling, but during the solidification process at pilot plant scale no subcooling was detected (Fig. 3). Knowing that no subcooling appeared with hydroquinone, the next step was to evaluate d-mannitol as PCM even though this PCM presented high subcooling in the DSC tests. However, the solidification process in the pilot plant scale presented high subcooling (Fig. 4), which obviously is really negative for any real application and much more for solar cooling applications which need to work in a narrow range of temperature.

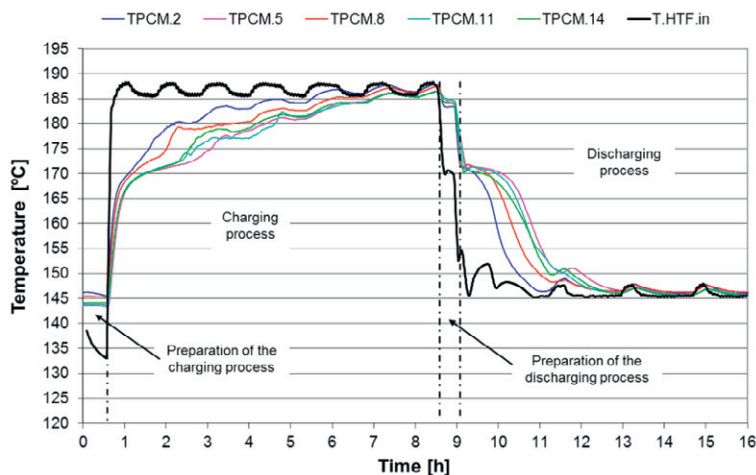


Fig. 3. Temperatures in the storage tank when hydroquinone is used as PCM

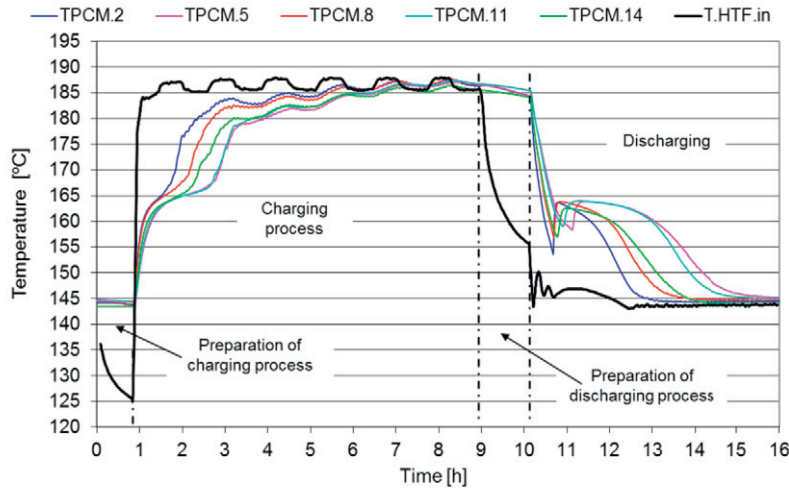


Fig. 4. Temperatures in the storage tank when d-mannitol is used as PCM

During the charging process, the energy balance equation of the whole storage tank can be written as equation 1 shows. The discharging process can be treated in an analogue way.

$$Q_{HTF} = Q_{PCM} + Q_{tank} + Q_{loss} + Q_{acc\ HTF} + Q_{insulation} \quad (1)$$

where Q_{HTF} is the energy given by the HTF during the charging process, Q_{PCM} is the energy stored by the PCM, Q_{tank} is the energy stored by the tank material (stainless steel), Q_{loss} is the total energy that was lost from the storage tank to the ambient and the floor of the pilot plant during the process, $Q_{acc\ HTF}$ is the accumulated energy by the HTF inside the storage tank, and $Q_{insulation}$ is the heat accumulated in the insulation materials. $Q_{acc\ HTF}$ could be neglected due to the low quantity of HTF inside the tubes, and due to the low C_p of the insulation materials $Q_{insulation}$ could be neglected as well.

Fig. 5 shows the HTF temperature at the inlet ($T_{HTF.in}$) and outlet ($T_{HTF.out}$) of the storage tank and the difference between them (Delta T) when hydroquinone was used as PCM during the charging process. From these values and knowing the HTF flow rate, the total heat given by the HTF to the PCM can be known (Equation 2). Notice that the charging process is done after 5.5 hours even if the experimentation let 8 hours to complete the melting process.

$$Q_{HTF} = \dot{m}_{HTF} \cdot \overline{C_{p,HTF}} \cdot (T_{HTF.in} - T_{HTF.out}) \quad (2)$$

As the PCM temperature is not the same along the storage tank, the tank was divided in 27 control volumes where the temperature in each of them is known. The control volumes are defined as the amount of PCM material that can be associated to every temperature sensor. Consequently, the temperature of this amount of PCM was considered to be the same as the sensor measuring it. Then the energy stored by the PCM had to be calculated depending if the PCM was in solid, liquid or in the phase change transition (Equation 3):

$$Q_{PCM} = M \cdot C_{p,s} \cdot (T_{PC} - T_{PCM.initial}) + M \cdot \Delta H_{PCM} + M \cdot C_{p,l} \cdot (T_{PCM.final} - T_{PC}) \quad (3)$$

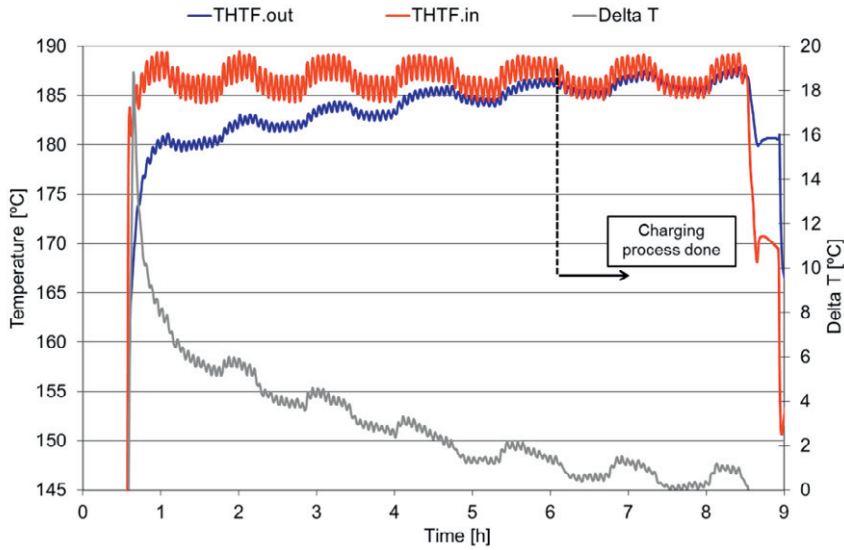


Fig. 5. Inlet and outlet HTF temperature of the storage tank during the charging process when hydroquinone is used as PCM

The energy that is stored in the storage tank by itself (stainless steel) is calculated using equation 4:

$$Q_{\text{tank}} = M \cdot \overline{C_{p,\text{steel}}} \cdot \overline{T_{\text{steel}}} \quad (4)$$

Finally the energy lost during all the process, which is lost by convection through the lateral walls and the top part of the tank to the ambient (5) and conduction which is from the bottom of the tank to the floor (6) can be calculated with equation 7:

$$\dot{Q}_{\text{loss,conv}} = \frac{(T_{\text{wall}} - T_{\text{ambient}})}{\frac{\Delta x_{\text{tank}}}{k_{\text{tank}} \cdot A_{\text{tank,w}}} + \frac{\Delta x_{\text{insulation}}}{k_{\text{insulation}} \cdot A_{\text{insulation}}} + \frac{1}{h_{\text{conv}} + A_{\text{insulation}}}} \quad (5)$$

$$\dot{Q}_{\text{loss,cond}} = \frac{(T_{\text{bottom}} - T_{\text{floor}})}{\frac{\Delta x_{\text{tank}}}{k_{\text{tank}} \cdot A_{\text{tank,b}}} + \frac{\Delta x_{\text{insulation}}}{k_{\text{insulation}} \cdot A_{\text{insulation}}}} \quad (6)$$

$$Q_{\text{loss}} = (\dot{Q}_{\text{loss,conv}} + \dot{Q}_{\text{loss,cond}}) \cdot \Delta t \quad (7)$$

Therefore, using those equations, the energy given by the HTF and the energy stored by the PCM during charging and discharging can be calculated from the experimental data. Fig. 6 shows the stored energy (ΔE) during the charging process when hydroquinone was used as PCM. Notice that the energy lost due to the heat losses and the energy stored by the stainless steel (storage tank) during the charging process are much lower than the energy stored by the PCM. From these data, the effective heat transfer of the storage tank during a charging process can be calculated (Equation 8). On the other hand, the effective heat transfer during the discharging process is calculated with equation 9.

$$\varepsilon_{cha} = \frac{Q_{PCM}}{Q_{HTF}} \quad (8)$$

$$\varepsilon_{dis} = \frac{Q_{HTF}}{Q_{PCM} + Q_{steel}} \quad (9)$$

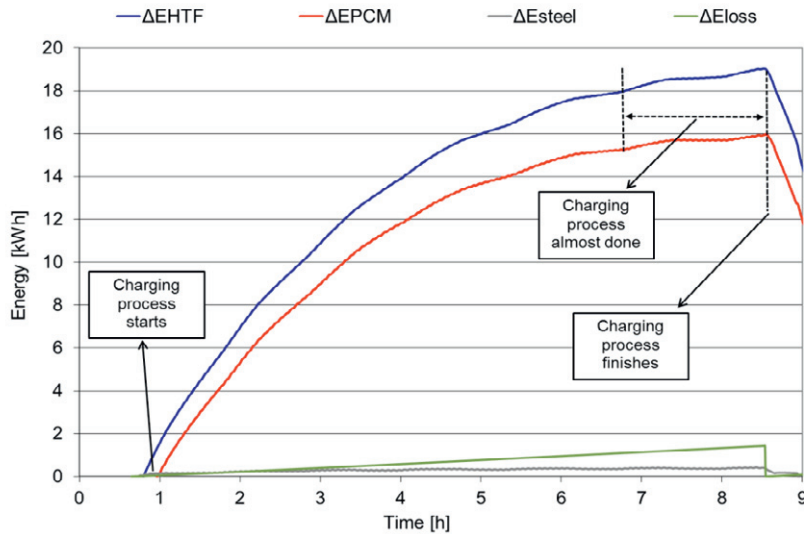


Fig. 6. Stored energy during the charging process when hydroquinone is used as PCM

Table 2 shows the main results of the experimentation performed using both hydroquinone and d-mannitol as PCM. The effective heat transfer from the HTF to the PCM during charging and vice versa, during the discharging process, is close to 1, therefore, almost all the heat that is given by the HTF during the charging process is recovered when the discharging occurs. When hydroquinone was used as PCM the effective heat transfer was 0.86, while it was 0.88 when d-mannitol was used.

Table 2. Main results of both charging and discharging processes using hydroquinone and d-mannitol as PCM

	Hydroquinone		D-mannitol	
	Charging	Discharging	Charging	Discharging
Time [min]	476	362	486	354
ΔE_{HTF} [kWh]	21.5	17.9	27.7	21.4
ΔE_{PCM} [kWh]	19.2	18.1	25.3	21.5
ΔE_{loss} [kWh]	1.4	1.2	1.3	0.8
ΔE_{steel} [kWh]	0.8	0.5	0.9	0.5
ε [-]	0.9	0.96	0.91	0.97

Notice that the time to complete both the charging and the discharging process of both PCM are almost the same. In both cases the time needed to complete the discharging process is lower than the charging. However, the process is not linear and in order to accumulate or give (melting or solidification) the 90% of the total heat of the PCM only 60% and 78% of the time is needed when hydroquinone was used and 69% and 58% when d-mannitol was used as PCM for charging and discharging processes, respectively.

Fig. 7 shows the energy stored by the PCM during the charging process and the energy released to the HTF when the PCM solidifies. Obviously, due to heat losses to the ambient during the period between both processes, the energy given by the PCM to the HTF is always lower than the energy accumulated during the melting of the PCM. Notice that for the same boundary conditions (initial PCM temperature and HTF inlet temperature) the energy stored by d-mannitol was higher, in particular, the enhancement was about 30% and 20% during the charging and the discharging processes, respectively.

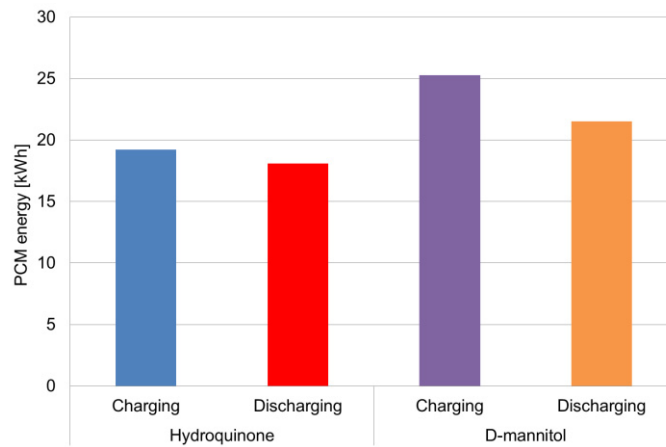


Fig. 7. Energy accumulated and given by both PCM during charging and discharging processes

4. Conclusions

This paper presents the development of a high temperature thermal energy storage (TES) system with latent heat materials at pilot plant scale. The TES system is targeted for solar cooling applications. To undertake this objective a flexible high temperature pilot plant was built, moreover a TES system based on shell-and-tubes heat exchanger configuration was designed and built at the University of Lleida.

Literature and DSC research of many phase change materials (PCM) candidates for solar cooling applications and selection and characterization of the adequate PCM were done. Hydroquinone and d-mannitol were the PCM selected to test them at pilot plant scale. Different charging and discharging experiments with different flow rates and heat transfer fluid (HTF) temperatures were performed to analyze the viability of the materials selected as PCM for solar cooling applications. For both PCM, no hysteresis was detected, and even though hydroquinone presented subcooling in the DSC, it did almost not appear in pilot plant scale, however, when d-mannitol was used big subcooling was detected during the discharging process.

An effective heat transfer coefficient between the storage material and the heat transfer fluid (HTF) was calculated. When hydroquinone was used as PCM the effective heat transfer was 0.86, while it was 0.88 when d-mannitol was used. Therefore, almost all the heat that is given by the HTF during the charging process is recovered when the discharging occurs.

For the same boundary conditions, the energy stored by d-mannitol was higher than that for hydroquinone; in particular, the enhancement was about 30% and 20% during the charging and the discharging processes even though the enhancement of the latent heat was only 10 and 16%, respectively.

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References

- [1] Chidambaram LA, Ramana AS, Kamaraj G, Velraj R. Review of solar cooling methods and thermal storage options. *Renewable and Sustainable Energy Reviews* 2011;15:3220-3228.
- [2] Gil A, Medrano M, Martorell I, Lázaro A, Dolado P, Zalba B, Cabeza LF. State of the art on high temperature thermal energy storage for power generation. Part 1-Concepts, materials and modellization. *Renewable and Sustainable Energy Reviews* 2010;14:31-55.
- [3] Medrano M, Gil A, Martorell I, Potau X, Cabeza LF. State of the art on high-temperature thermal energy storage for power generation. Part 2-Case studies. *Renewable and Sustainable Energy Reviews* 2010;14:56-72.
- [4] Medrano M, Yilmaz MO, Nogués M, Martorell I, Roca J, Cabeza LF. Experimental evaluation of commercial heat exchangers for use as PCM thermal storage systems. *Applied Energy* 2009;86:2047-2055.
- [5] Adine HA, Qarnia HE. Numerical analysis of the thermal behaviour of a shell-and-tube heat storage unit using phase change materials. *Applied Mathematical Modelling* 2009;33:2132-2144.
- [6] Trp A, Lenic K, Frankovic B. Analysis of the influence of operating conditions and geometric parameters on heat transfer in water-paraffin shell-and-tube latent thermal energy storage unit. *Applied Thermal Engineering* 2006;26:1830-1839.
- [7] Tao YB, He YL. Numerical study on thermal energy storage performance of phase change material under non-steady-state inlet boundary. *Applied Energy* 2011;88:4172-4179.
- [8] Agyenim F, Eames P, Smyth M. Heat transfer enhancement in medium temperature thermal energy system using a multitube heat transfer array. *Renewable Energy* 2010;35:197-207.
- [9] Bayón R, Rojas E, Valenzuela L, Zarza E, León J. Analysis of the experimental behavior of a 100 kWth latent heat storage system for direct steam generation in solar thermal power plants. *Applied Thermal Engineering* 2010;30:2643-2651.
- [10] Zalba B, Marín JM, Cabeza LF, Mehling H. Review on thermal energy storage with phase change: Materials, heat transfer analysis and applications. *Applied Thermal Engineering* 2003;23:251-283.
- [11] Sharma SD, Sagara K. Latent heat storage materials and systems: A review. *International Journal of Green Energy* 2005;2:1-56.